AD-A167 666   SEMICONDUCTOR/SOLID ELECTROLYTE JUNCTIONS FOR OPTICAL   1/1
                INFORMATION STORAGE (U) ELTRON RESEARCH INC AURORA IL
                A F SAMMELLS ET AL. 15 MAY 86 N00014-84-C-0723

UNCLASSIFIED   F/G 7/4   NL
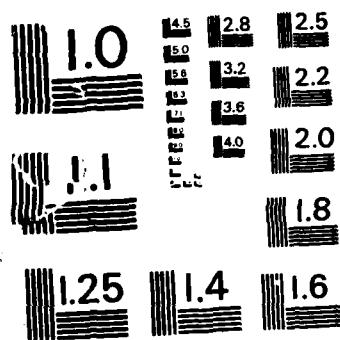
MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

AD-A167 666

OFFICE OF NAVAL RESEARCH

CONTRACT NO. N00014-84-C-0723

INTERIM TECHNICAL REPORT 0001AH

SEMICONDUCTOR/SOLID ELECTROLYTE JUNCTIONS FOR OPTICAL
INFORMATION STORAGE.
ELECTROCHROMIC EFFECTS ON HEPTYLVIOLOGEN INCORPORATED WITHIN A
SOLID POLYMER ELECTROLYTE CELL

By

Anthony F. Sammells and Nirupama U. Pujare

DTIC
ELECTE
MAY 1 3 1986
S
D
D

DTIC FILE COPY

86 5 13 028

ELTRON RESEARCH INC.

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER 0001AH	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) SEMICONDUCTOR/SOLID ELECTROLYTE JUNCTIONS FOR OPTICAL INFORMATION STORAGE. ELECTROCHROMIC EFFECTS ON HEPTYLVIOLOGEN INCORPORATED WITHIN A SOLID POLYMER ELECTROLYTE CELL.		5. TYPE OF REPORT & PERIOD COVERED Technical January 16, 1986 May 15, 1986
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Anthony F. Sammells and Nirupama U. Pujare		8. CONTRACT OR GRANT NUMBER(s) N00014-84-C-0723
9. PERFORMING ORGANIZATION NAME AND ADDRESS ELTRON RESEARCH INC. 4260 Westbrook Drive Aurora, IL 60505		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NR 627-826
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research/Chemistry Program Arlington, VA 22217		12. REPORT DATE May 15, 1986
		13. NUMBER OF PAGES
14. MONITORING AGENCY NAME & ADDRESS(If different from Controlling Office)		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
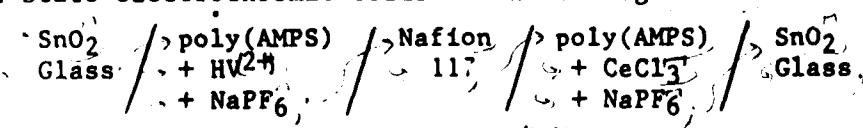
16. DISTRIBUTION STATEMENT (of this Report)

Approved for Public Release: Distribution Unlimited

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

Accepted for publication in the Journal of Electrochemical Society.

18. SUPPLEMENTARY NOTES

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Solid-state electrochromic cells of the configuration

$$\text{SnO}_2 \text{ Glass} / \text{poly(AMPS)} + \text{HV}^{2+} + \text{NaPF}_6 / \text{Nafion } 117 / \text{poly(AMPS)} + \text{CeCl}_3 + \text{NaPF}_6 / \text{SnO}_2 \text{ Glass}$$

were prepared. Upon subjecting the (HV^{2+}) working electrode compartment to a cathodic scan, two distinct reduction peaks were observed at respectively -1.74 and -1.90V versus the CeCl$_3$/SnO$_2$ reference/counter electrode. This corresponded to the formation

DD FORM JAN 73 1473   EDITION OF 1 NOV 53 IS OBSOLETE

· 20. <u>ABSTRACT</u> Continued

of respectively, the radical and diradical cation species of HV^{2+}. This
electrochromic cell was found to be highly electrochemically reversible as
monitored by a (He/Ne) laser beam (583nm) transmitted through the bulk of
this semi-transparent thin film solid-state cell.

Cells were also prepared using $n-TiO_2$ as the working electrode in contact
with the HV^{2+} compartment. A progressive trend to more negative $n-TiO_2$
flat band potentials (V_{FB}) was observed between the initially prepared cell
and the first and second electrochemically formed HV^{2+} radical cation species.

Accesion For		
NTIS CRA&I	☑	
DTIC TAB	☐	
Unannounced	☐	
Justification		
By		
Dist ibution /		
Availability Codes		
Dist	Avail and / or Special	
A-1		

TABLE OF CONTENTS

iv

ELTRON RESEARCH INC.

LIST OF FIGURES

ELTRON RESEARCH INC.

EXPERIMENTAL

Electrochemical measurements were performed using either a Stonehart Associates BC 1200 or a Wenking LT 78 potentiostat controlled by a BAS Model CV-1B cyclic voltammetry unit. Current-voltage data were recorded on a Houston Instruments Omnigraphic Model 154-046 X-Y recorder.

Single crystal $n-TiO_2$ was initially heated under hydrogen at 800°C for several hours to enhance its n-doping characteristics. Ohmic contact to the back surface of the crystal was made by the introduction of gallium-indium eutectic into the freshly etched ($c.H_2SO_4$) surface. Current collection was accomplished with a nichrome wire and silver epoxy (Epoxy Technology, Inc.), and the assembly cured at 150°C for 1 hour. Current collection to the SnO_2 conducting glass was also performed as above. Conductance and capacitance measurements for admittance spectroscopy analysis of the polymer-semiconductor interface from which $n-TiO_2$ V_{FB} values were obtained were performed using an HP-4276A digital LCZ meter between 100 and 20kHz.

1

RESULTS AND DISCUSSION

There has been a continuous interest over the last several years to investigate the viologens[1] as the basis for electrochromic alphanumeric displays using both aqueous and non-aqueous liquid electrolytes[2-4]. These materials are based upon the alkyl derivatives of 4,4' dipyridyl. Electrochemical reduction of, for example, 1,1' diheptyl-4,4' bipyridyl (heptyl viologen) dibromide in aqueous KBr containing electrolyte, has been shown to result in the formation of insoluble red radical and diradical cation species at the cathode[5,6]. These processes have been found dependent upon both the anion present in the supporting electrolyte and the cathode material used as a substrate for the reduced heptyl viologen radical species. For example, stable red deposits have been obtained on platinum electrodes in fluoride or sulfate containing electrolytes, whereas no color change is observed when gold is used as the cathode[5]. Electrochromic devices based upon these electrochemically reversible viologen redox couples would greatly benefit by their incorporation within solid-state solid polymer electrolyte (SPE) cells. By this means, relatively thin displays might be feasible compared to their aqueous electrolyte analogs.

Here we wish to discuss some recent work from our laboratory on solid-state electrochromic cells in which heptyl viologen (HV^{2+}) was initially incorporated within the homopolymer poly-2-acylamido-2-methyl propane sulfonic acid (poly(AMPS)). In this cell, separation between the electrochromic working electrode (HV^{2+} in poly(AMPS)) and the reversible counter electrode ($CeCl_3$ in poly(AMPS)) was achieved by using the insoluble copolymer perfluorosulfonic acid (Nafion). Current collection from each electrode compartment was via the use of SnO_2 conducting glass. The solid-state cell configuration used in this work can be represented by:

SnO_2 Glass	/	poly(AMPS) + HV^{2+} + $NaPF_6$	/	Nafion 117	/	poly(AMPS) + $CeCl_3$ + $NaPF_6$	/	SnO_2 Glass
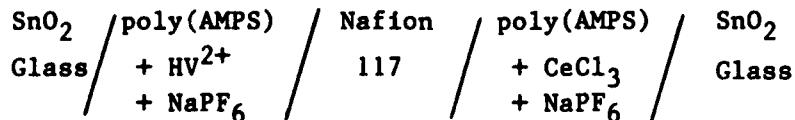
These cells were prepared by applying a thin coating ($\simeq$ 2 microns) of poly(AMPS) (as a 10^w/o solution) containing 0.04M HV^{2+} and 0.001M $NaPF_6$ as a supporting electrolyte, onto a SnO_2 conducting glass substrate electrode. This electrode was permitted to initially dry for an hour. This was followed

2

ELTRON RESEARCH INC.

by being directly contacted to an initially Na^+ exchanged Nafion 117 membrane. The counter electrode used in this cell consisted of a similar poly(AMPS) film introduced onto a SnO_2 conducting glass electrode, possessing 0.04M $CeCl_3$ to maintain redox electrochemistry upon cycling and 0.001M $NaPF_6$ as a supporting electrolyte.

Both of the above half-cells were pressed together and the resultant solid-state cell permitted to dry a further 30 minutes. This cell was then subjected to cyclic voltammetry (CV) measurements as shown in Figure 1. The logistics associated with these thin SPE cells inhibited the convenient intro- duction of a reference electrode. As a consequence, electrochromic working electrode potentials were recorded as a function of the $CeCl_3$ containing SnO_2 conducting glass electrode compartment. Upon subjecting the working electrode compartment to an initial cathodic scan, two distinct reduction peaks were observed at respectively -1.74 and -1.90V versus the $CeCl_3/SnO_2$ glass electrode compartment. The initial reduction peak at 1.74V resulted in the appearance of a distinct violet film which became darker at the second reduction potential (-1.9V).

Upon subjecting the electrochromic working electrode to a subsequent anodic scan, two corresponding oxidation peaks were observed at -1.82 and -1.0V resulting in the complete removal of the violet color. The two initial reduction peaks corresponded to the formation of, respectively, the radical and diradical cation species of heptyl viologen resident within the poly(AMPS), presumably located in close proximity to the SnO_2 electrode. Further anodic scan past the initial open-circuit potential (which was typically in the $\cong$ 100mV range) resulted in an oxidation peak at 1.6V. This latter peak was probably associated with the Ce^{3+}/Ce^{+4} redox couple within the counter elec- trode compartment.

The observation by others[4] that the half-wave potential for HV^{2+} reduc- tion is dependent upon the nature and concentration of anion species within the supporting electrolyte is related to the solubility produce to the re- duced radical cation species as defined by the product $(dipy^+)$ (X^-). It is precipitation of this red or violet species at or within close proximity of the cathode substrate which is responsible for the observed electrochromic effects in SPE cells discussed here. The initial electrochemical reduction step occurring in this cell lending to the radical cation can be represented

3

by:

$$dipy^{2+} + PF_6^- \quad \rightleftarrows \quad dipy^+$$

which is followed by chemical formation of the colored reaction product via

$$dipy^+ + PF_6^- \quad \rightleftarrows \quad dipyPF_6$$

This can, in part, explain the significantly different redox potentials found for HV^{2+} reduction in acetonitrile (where the reduced radical cation is soluble) and water[7] where in the latter electrolyte, strong association with anionic species can occur leading to precipitation. The second reduction step leading to the formation of the diradical species can be represented by:

$$dipy^+ + e^- \quad \rightleftarrows \quad dipy$$

The observed more intense electrochromic effect during the second reduction process was probably due to the simultaneous and continuous formation of the initial radical species at this more negative potential region.

The electrochemical reversibility of this electrochromic effect was investigated by monitoring changes in the relative absorption of an initially 1mW He/Ne laser beam (583nm) after being passed directly through this thin SPE cell, as a function of applied potential. The transmitted laser beam intensity was detected using a Hamamatsu PIN photodiode amplified by an RCA 3140 Op. Amp. Figure 2 summarizes the electrochemical cycling characteristics of these electrochromic cells as a function of varying potentiostatted charge/ discharge voltages. These were varied between ± 0.75V (curve a), ± 1.0V (curve b), ± 1.25V (curve c), ± 1.5V (curve d) and ± 2.0V (curve e). Preliminary cells have demonstrated excellent reversibility in excess of a hundred cycles.

To investigate the influence of heptyl viologen and its reduced radical cation species on the $n-TiO_2/HV^{2+}$, poly(AMPS) solid-state junction, cells of the general configuration

$$n-TiO_2 \Big/ \begin{array}{c} poly(AMPS) \\ + HV^{2+} \\ + NaPF_6 \end{array} \Big/ \begin{array}{c} Nafion \\ 117 \end{array} \Big/ \begin{array}{c} poly(AMPS) \\ + CeCl_3 \\ + NaPF_6 \end{array} \Big/ \begin{array}{c} SnO_2 \\ glass \end{array} \Big/$$
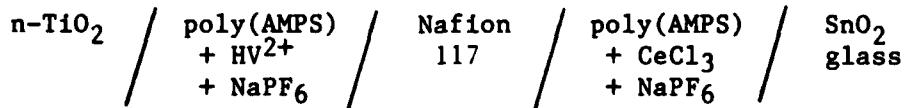
were prepared. A typical CV from this cell is summarized in Figure 3. Because of the lower electronic conductivity of $n-TiO_2$ compared to SnO_2 coated glass, the diradical cation reduction peak is not readily discernable upon initial cathodic sweep. Formation of radical and diradical species become

4

evident however upon subsequent anodic sweep by a shoulder at $\cong$ -2.25V and a peak at -1.35V vs. the $CeCl_3/SnO_2$, reference/counter electrode. Again, the electrochromic effect at the interface was found to be reversible and distinct as with the previously discussed electrochemical cell. n-TiO_2, V_{FB} values were measured from impedance and admittance measurement techniques by use of the appropriate equivalent circuit representative of the n-TiO_2/HV^{2+} interface region. Here parameters measured were based upon resistive or capacitive elements arranged in either series or parallel configurations. The magnitude of these parameters were dependent upon the measurement frequency. This is in comparison to the equivalent circuit elements[8] which are passive and can be used to gain information on surface-state energies and Faradaic charge transfer rates, etc. As we have discussed previously, a technique has been developed for the measurement of frequency independent Mott-Schottky parameters[9]. This technique was used to obtain Mott-Schottky data from which V_{FB} values for n-TiO_2 at its interface with reduced HV^{2+} species could be determined. In this analyses, the double layer capacitance (C_{dl}) was assumed to be much larger than C_{sc} (i.e. $C_{dl} >>> C_{sc}$) although some components of C_{dl} may be present in the measured C_{sc} values. The simplest equivalent circuit configuration of the semiconductor/SPE interface region consists of the space charge capacitance (C_{sc}) connected in series with the bulk conductance G_B[11] (Figure 4). The admittance of this circuit was given by the equation:

$$Y_x = \frac{\omega^2 G_B C_{sc}^2 + J\omega G_B^2 C_{sc}}{G_B^2 + (\omega C_{sc})^2}$$

where ω is the angular frequency ($2\pi f$). The measured parameters, Gp (parallel conductance) and Cp (parallel capacitance) were obtained directly using an HP-4276 LCZ meter. The related admittance was obtained by use of the relationship:[9]

$$Y_z = Gp + j \omega Cp$$

Relating the real and imaginary components of Y_x and Y_z gives:

$$Cp/\omega = \frac{\omega C_{sc}^2 G_B}{G_B^2 + (\omega C_{sc})^2}$$

and

$$\omega Cp = \frac{\omega G_B^2 C_{sc}}{G_B^2 + (\omega C_{sc})^2}$$

5

Plots of Gp/ω vs. ω and ωCp vs. ω will exhibit maxima at a frequency $\omega_{max} = G_B/C_{sc}$ and the desired parameters C_{sc} and G_B can be obtained through the following relationships:

$$Gp/\omega_{max} = C_{sc}/2$$

and

$$\omega Cp_{max} = G_B/2$$

C_{sc} obtained in this manner was frequency independent and thus a plot of C_{sc} values obtained at varying bias voltages yielded frequency independent Mott-Schottky plots for the determination of V_{FB}.

Figures 5-7 compare Mott-Schottky data obtained using this technique for the $n-TiO_2/HV^{2+}$, poly(AMPS) interface region for respectively the as made junctions (Figure 5), after electrochemical reduction of HV^{2+} to the radical cation by potentiostatting at -1.35V (Figure 6), and after reduction to the diradical cation at -2.25V. All potentials were measured versus the $CeCl_3$/poly(AMPS) counter/reference electrode. As can be seen from this data, there is a progressive trend to more negative V_{FB} values for $n-TiO_2$ as HV^{2+} is reduced. Similar observations are found with liquid-junction PEC cells using $n-TiO_2$ as an electrode.

ELTRON RESEARCH INC.

REFERENCES

1. L. Michaelis, Z. Biochem., 250, 564 (1932)

2. C. J. Schoot, J. J. Ponjee, H. T. van Dam, R. A. van Doorn, and P. T. Bolwijn, Appl. Phys. Lett., 23, 64 (1973)

3. H. T. van Dam and J. J. Ponjee, J. Electrochem. Soc., 121, 1555 (1974)

4. H. T. van Dam, J. Electrochem Soc., 123, 1181 (1976)

5. R. S. Jasinski, J. Electrochem., 124, 637 (1977)

6. K. Belinko, Appl. Phys. Lett., 29, 363 (1976)

7. C. S. Johnson and H. S. Gutowsky, J. Chem. Phys., 39, 58 (1963)

8. V. Del Toro, "Principles of Electrical Engineering," Prentice-Hall, Englewood Cliffs, NJ (1972)

9. J. Dubow and R. Krishnar, "Novel Concepts in Electrochemical Solar Cells," SERI Final Report; Contract #XS-0-9272-1 Oct. (1981)

10. I. Lundstrom, M. S. Shivaraman and C. Svensson, J. Appl. Phys., 46 3876 (1975)

ELTRON RESEARCH INC.
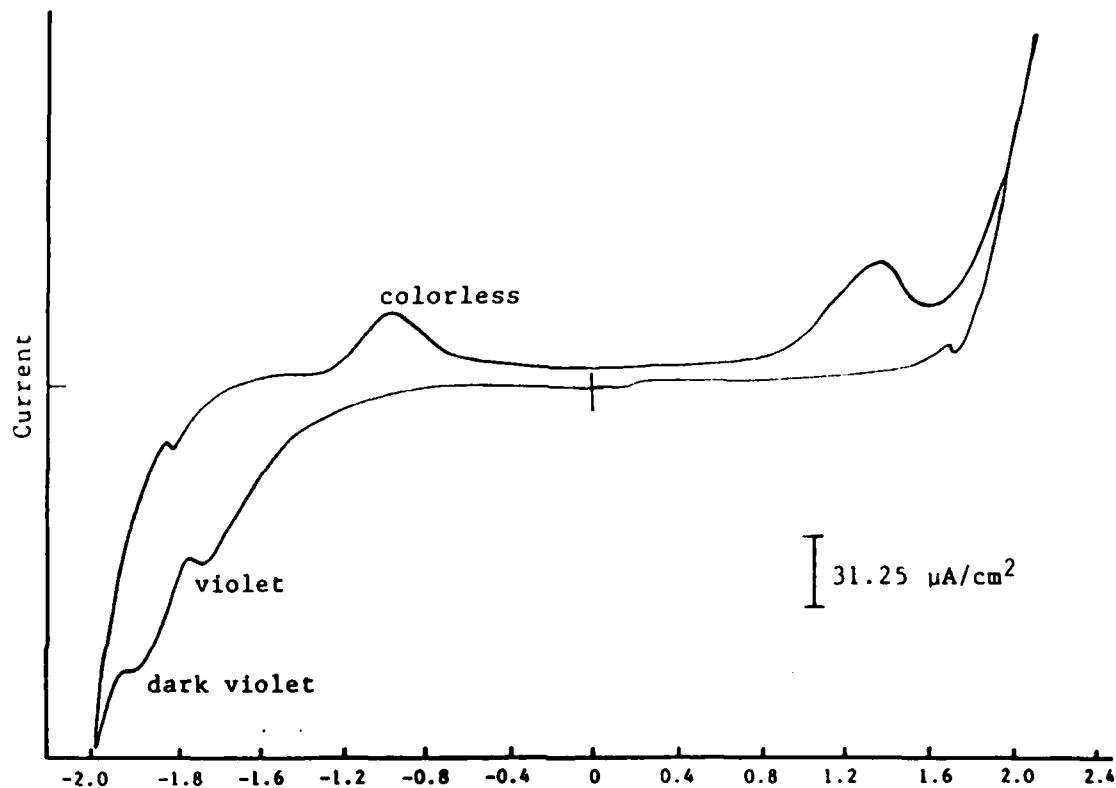
Electrode voltage (volts) vs. SnO_2 conducting glass. Reference/counter electrode.

<u>Figure 1</u>. CV of cell

Polyamps + 0.04M Heptyl viologen + 0.001M $NaPF_6$ on SnO_2 conducting glass / Nafion 117 membrane Na^+ / Polyamps + 0.04M $CeCl_3$ + 0.001M $NaPF_6$ on SnO_2 conducting glass

Sweep rate – 50mV/sec

8
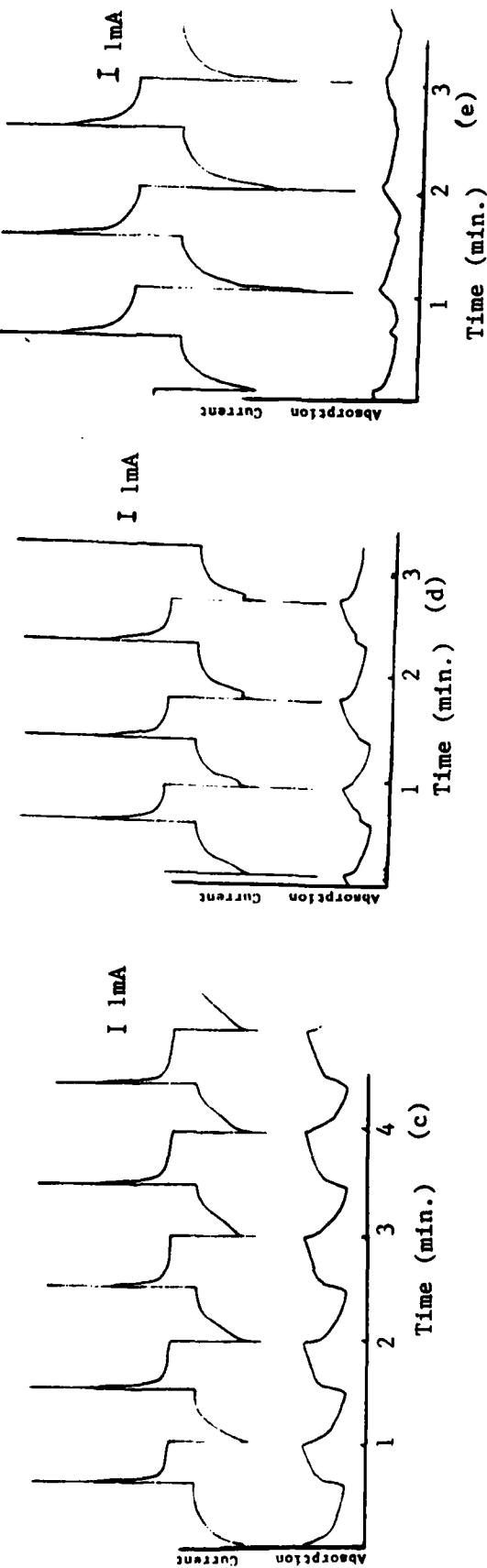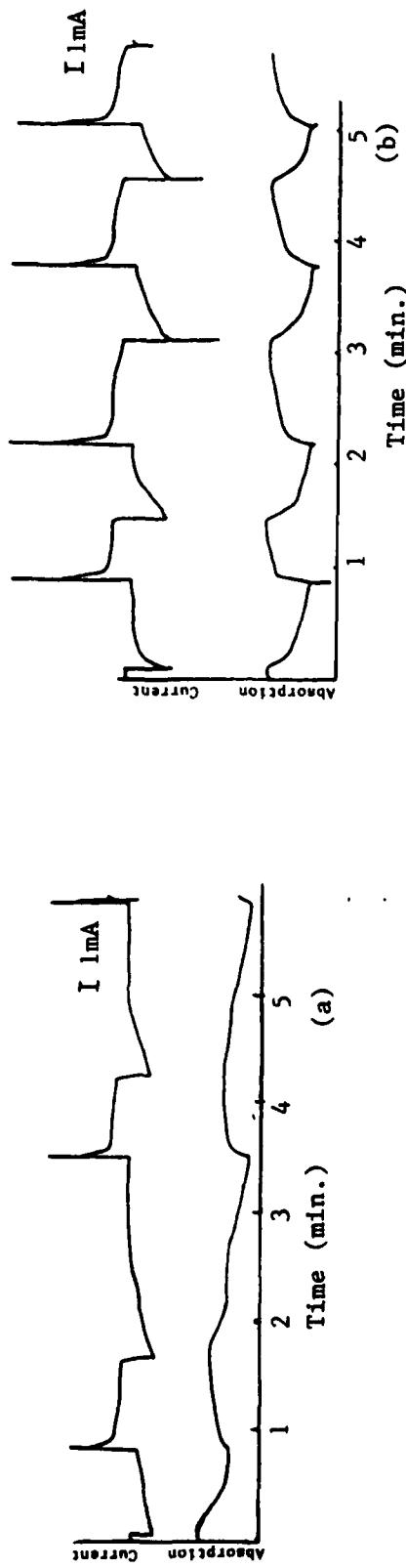
Figure 2. Charge/light absorption characteristics for the cell

SnO_2 cond. glass/0.04M Heptyl Viologen in / Nafion 117 / 0.04 M $CeCl_3$ in polyamps/SnO_2 cond. glass polyamps + 0.001 M $NaPF_6$ membrane + 0.001 M $NaPF_6$

Illumination source: He/Ne laser at 583 nm: Beam intensity: 1 mW. Potentiostatted at a) ± 0.75V, b) ± 1.0V, c) ± 1.25V, d) ± 1.5V, and e) ± 2.0V upon cycling.

9

ELTRON RESEARCH INC.
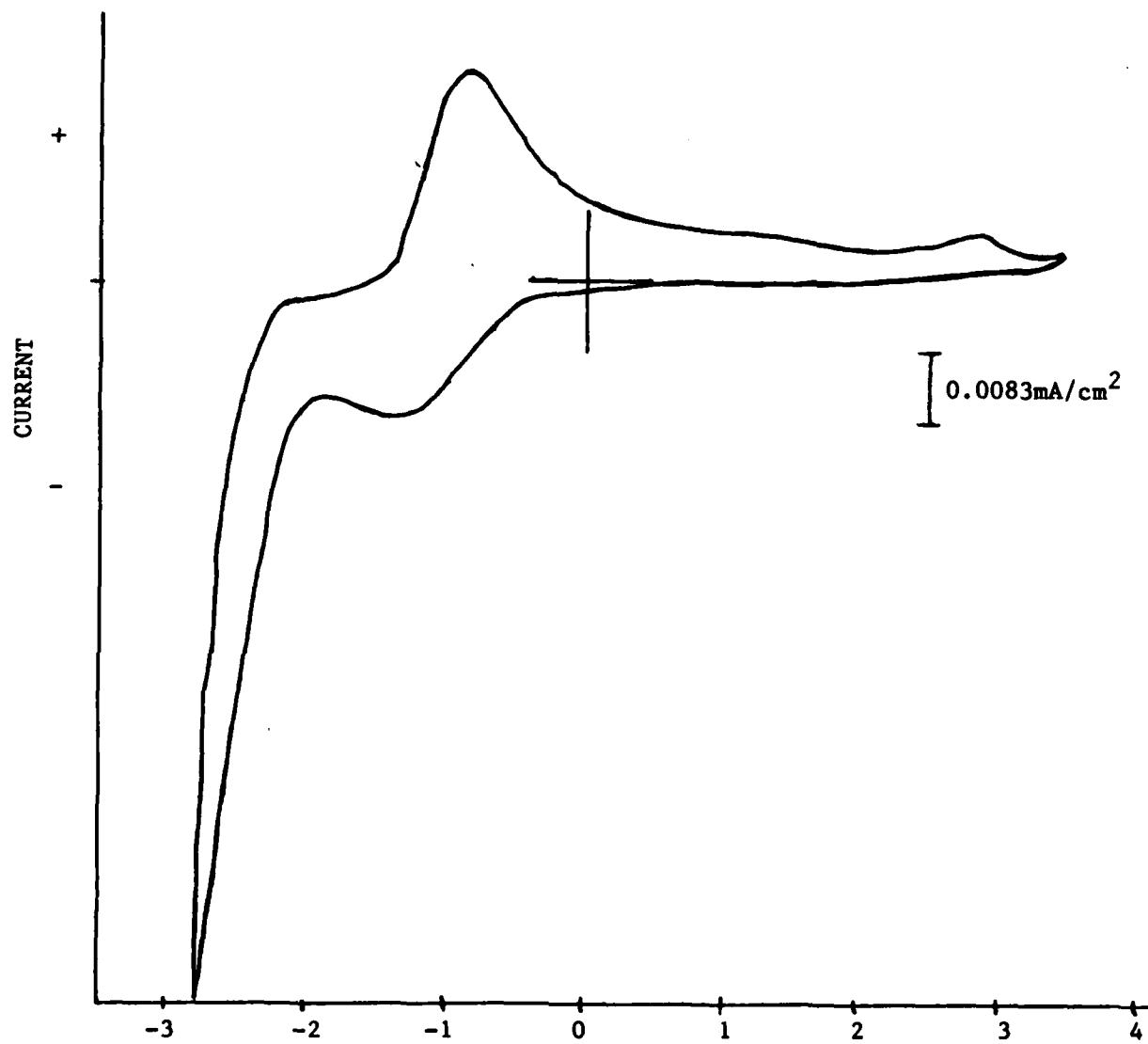
Electrode voltage (volts) vs. SnO_2 conducting glass reference/counter electrode.

Figure 3. Cyclic voltammogram of cell

n-TiO_2	0.04 M heptyl viologen in poly-AMPS + 0.001 M $NaPF_6$	Nafion 117 membrane Na^+	0.04 M $CeCl_3$ in poly-AMPS + 0.001 M $NaPF_6$	SnO_2 conducting glass

Sweep rate: - 50 mv/sec.

10
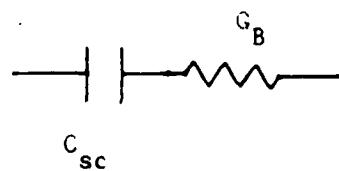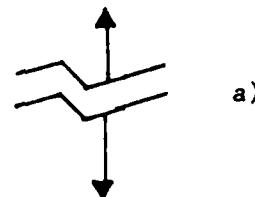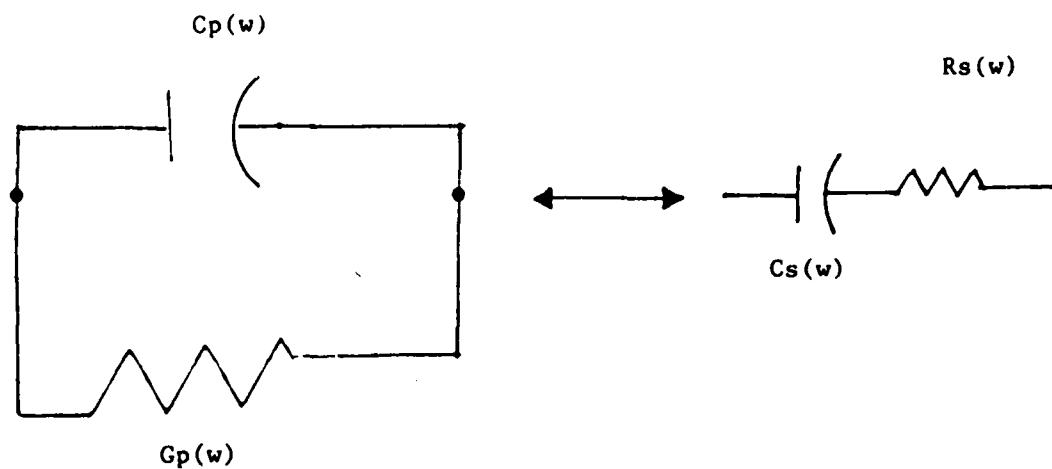
Figure 4. Passive element network for C_{sc} measurement in Mott-Schottky analyses.

    a) This transformation is performed by a successive reduction in the equivalent circuit representation of the semiconductor/SPE interface[10].

ELTRON RESEARCH INC.

y-axis: 1/CSC^2 (× 1E-11)

x-axis: VOLTAGE
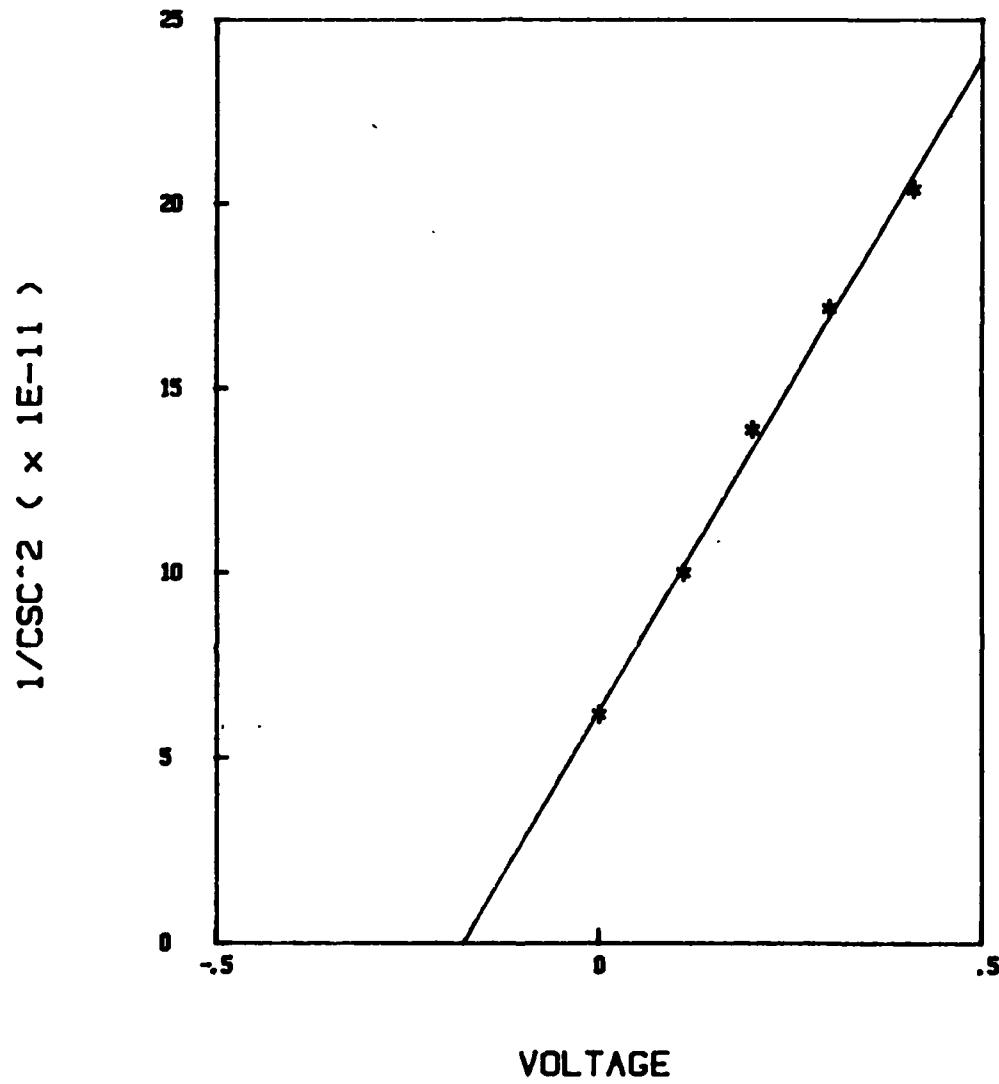
Figure 5. Mott-Schottky Plot of the cell.

| n-TiO$_2$ | 0.04 M Heptyl Viologen in poly-AMPS + 0.001 M NaPF$_6$ | Nafion 117 membrane Na$^+$ | 0.04 M CeCl$_3$ in poly-AMPS + 0.001 M NaPF$_6$ | SnO$_2$ conducting glass |

Before being subjected to electrochemical reduction V_{FB} for n-TiO$_2$ = -0.1801 V.

12
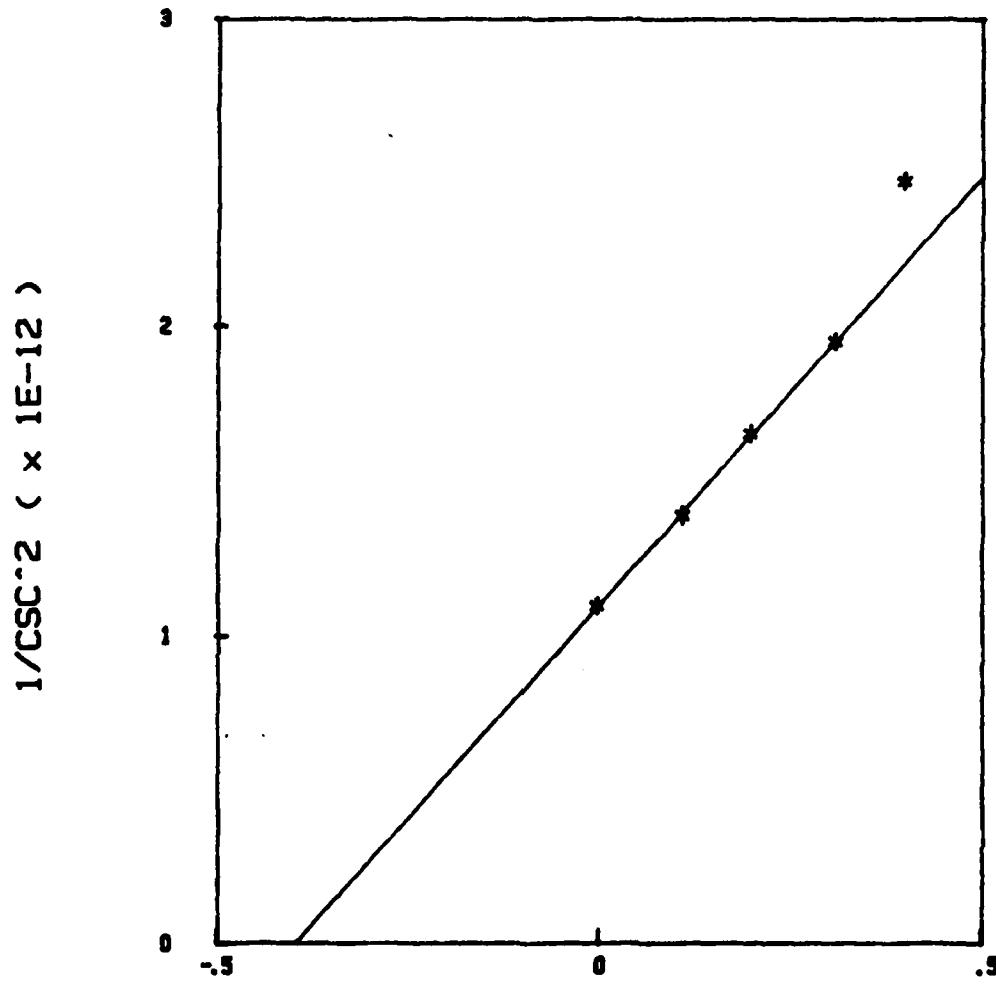
Figure 6. Mott-Schottky plot of the cell

| n-TiO$_2$ | 0.04M heptyl viologen in poly-AMPS + 0.001 M NaPF$_6$ | Nafion 117 membrane Na$^+$ | 0.04M CeCl$_3$ in poly-AMPS + 0.001 M NaPF$_6$ | SnO$_2$ Conducting Glass |

After being reduced at -1.35V corresponding to the radical cation.

$$V_{FB} \text{ for n-TiO}_2 = -0.3951V$$

13
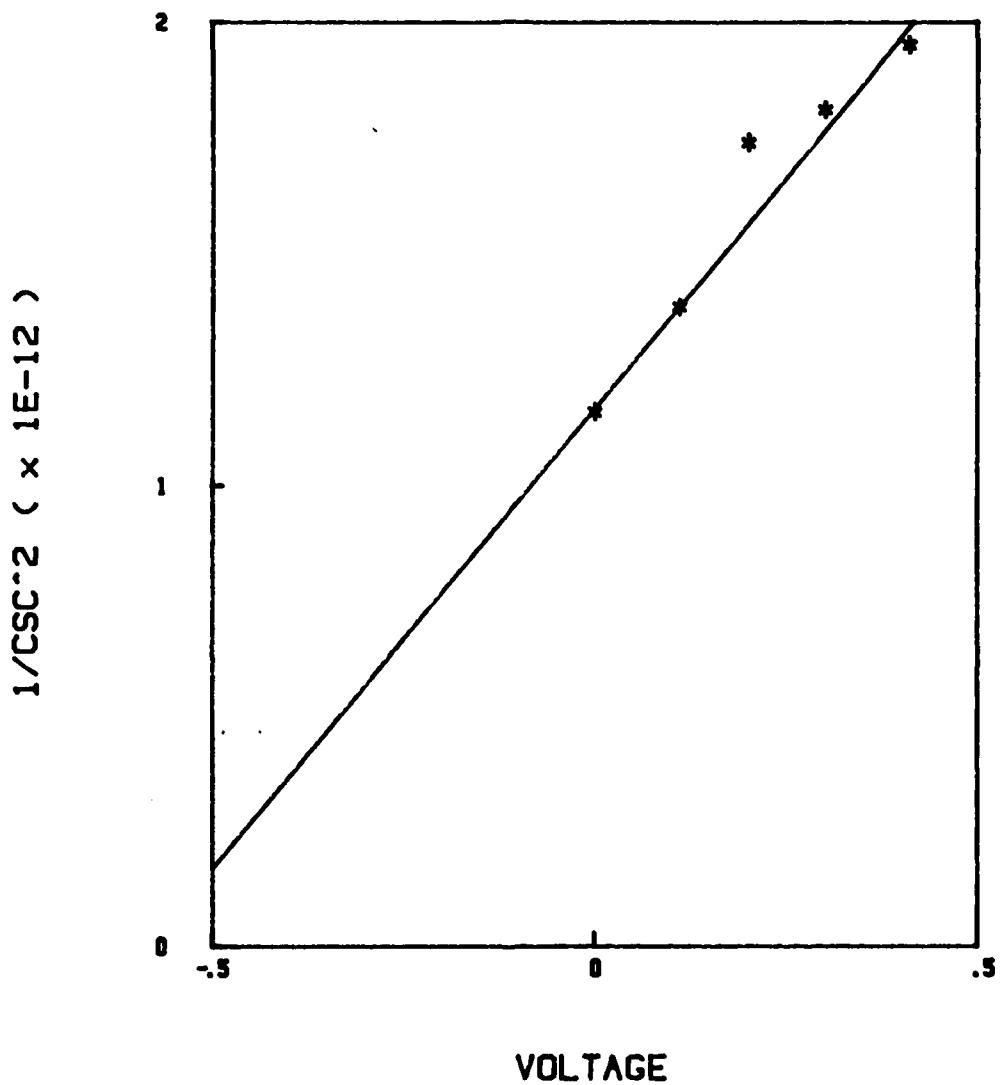
Figure 7. Mott-Schottky plot of the cell

| n-TiO$_2$ | 0.04M Heptyl Viologen in poly-AMPS + 0.001 M NaPF$_6$ | Nafion 117 membrane Na$^+$ | 0.04 M CeCl$_3$ in poly-AMPS + 0.001M NaPF$_6$ | SnO$_2$ Conducting Glass |

After being reduced at -2.25V corresponding to the diradical cation.

V_{FB} for n-TiO$_2$ = -0.5916V

14

ELTRON RESEARCH INC.

END

DTIC

6-86